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Docket No. 12003023

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Mail Stop PROVISIONAL PATENT APPLICATION
Commissioner for Patents
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TRANSMITTAL OF PROVISIONAL APPLICATION
PURSUANT TO 37 CFR § 1.53(c)

Application of: David Jarus

whose address is: 33587 Walker Road, Avon Lake, OH 44102

For: Nanoconcentrates Containing Polyolefin Elastomer

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1. Enclosed is a new provisional patent application. It includes 10 pages of text and 0 page(s) of drawings.

2. Please charge Deposit Account No. 07-1077 in the amount of $160.00 for the fee pursuant to 37 CFR § 1.16(k). Please credit or debit that account as needed to complete the filing of the application.

3. Please address all correspondence relating to this application to the following address:

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Date 8 October 2003

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PATENT
File No. 12003023

Nanoconcentrates Containing Polyolefin Elastomer

Field of Invention

This application relates to polymer concentrates containing nanoclays.

Background of the Invention

Nanotechnology is an exciting new field of science. The use of intercalated phyllosilicates, also called smectite clays, particularly montmorillonite clays, has been recognized as valuable for reinforcing fillers.

Nanocor, Inc. is a leader in the field of making and selling montmorillonite nanoclays and concentrates of them where the clays are exfoliated. Further technical and commercial information can be found at www.nanocor.com.

One of the polymers into which montmorillonite nanoclay concentrates is thermoplastic polyolefin (TPO), particularly where the polyolefin is polypropylene (PP).

Summary of the Invention

One aspect of the invention is the utilization of polyolefin rubber in a nanoconcentrate which contains nanoclay.

Another aspect of the present invention is a method of making the nanocomposite wherein the polyolefin elastomer is added downstream in an extruder from where the other ingredients are added.

An advantage of the present invention is that a balance of stiffness and toughness is achieved using in a TPO the nanocomposites of the present invention prepared according to the method of the present invention. This balance of stiffness and toughness is superior to those of the TPO without nanoconcentrates therein.

Another advantage of the present invention is that the method delays addition of the polyolefin rubber until after the nanoclay is thoroughly dispersed in the concentrate carrier, usually PP. This delay, it is believed, assures that the nanoclay present is not as likely to become intermixed within the dispersed phase of polyolefin rubber. Thus, the valuable nanoclay can increase the benefit of its properties in the final article molded from a combination of TPO and the nanoconcentrate of the present invention.

Embodiments of the Invention

TPO's are commercially available from such multi-national sources as Basell Polyolefins. TPO's can have a variety of properties, ranging from rigid to flexible to impact-modified polyolefin copolymers along a continuum known to those skilled in the art. The final use of an article made from TPO benefits from these tailored properties.

Nanoclay is a clay from the smectite family. Smectites have a unique morphology, featuring one dimension in the nanometer range. Montmorillonite clay is the most common member of the smectite clay family. The montmorillonite clay particle is often called a platelet, meaning a sheet-like structure where the dimensions in two directions far exceed the particle's thickness.

Nanoclay becomes commercially significant if intercalated with an intercalant. An intercalate is a clay-chemical complex wherein the clay gallery spacing has increased, due to the process of surface modification by an intercalant. Under the proper conditions of temperature and shear, an intercalate is capable of exfoliating in a resin matrix. An intercalant is an organic or semi-organic chemical capable of entering the montmorillonite clay gallery and bonding to the surface. Exfoliation describes a dispersion of a surface treated nanoclay in a plastic matrix.

In exfoliated form, nanoclay platelets have a flexible sheet-type structure which is remarkable for its very small size, especially the thickness of the sheet.

The length and breadth of the particles range from 1.5 μm down to a few tenths of a micrometer. However, the thickness is astoundingly small, measuring only about a nanometer (a billionth of a meter). These dimensions result in extremely high average aspect ratios (75-500). Moreover, the miniscule size and thickness mean that a single gram contains over a million individual particles.

Nanocomposites are the combination of the surface treated nanoclay and the plastic matrix. In polymer compounding, a nanocomposite is a very convenient means of delivery of the nanoclay into the ultimate compound, provided that the plastic matrix is compatible with the principal polymer resin components of the compounds. In such manner, nanocomposites are available in concentrates, masterbatches, and compounds from Nanocor, Inc. of Arlington Heights, Illinois (www.nanocor.com) and PolyOne Corporation of Avon Lake, Ohio (www.polyone.com) in a variety of nanocomposites.

Nanocomposites offer flame-retardancy properties because such nanocomposite formulations burn at a noticeably reduced burning rate and a hard char forms on the surface. They also exhibit minimum dripping and fire sparkling.

When using Nanocor produced nanoclay, the amount of this additive in concentrate form can range from about 2 weight percent to about 50 weight percent, and preferably between about 3 and about 20 weight percent of the total compound. Upon addition to the compound, the intercalated nanoclay exfoliates with the addition of compatibilizers known to those skilled in the art. In a preferred embodiment, the compatibilizer is a grafted maleic anhydride such as disclosed in U.S. Pat. No. 5,717,500 (Karande et al.).

The preparation of nanoconcentrates uses extrusion mixing equipment known to those skilled in the art. But the present invention departs from convention in that the concentrate differs from the TPO to which is to be mixed. Conventionally, the concentrate is made by mixing TPO and nanoclay, and

optionally a compatibilizing dispersion agent such as maleated polypropylene (PP-g-MAH).

In the present invention, the TPO is not used in forming the concentrate. Rather, the constituents of the TPO, PP and an elastomer, particularly a polyolefin elastomer, are added separately and at different locations in the extruder. More specifically, the polyolefin elastomer is added downstream of the other ingredients, which gives the nanoclay and its optional dispersion agent both more time and less interference in dispersing completely within the polypropylene carrier.

Preferably, the mixing equipment is a co-rotating twin-screw extruder commercially available from Werner-Pfleiderer. The extruder should be capable of screw speeds ranging from about 50 to about 12,000 rpm. The temperature profile from the barrel number two to the die should range from about 170°C to about 270°C, and preferably from around 200°C for this nanoconcentrate. The nanoconcentrate can be pelletized for later use.

Polyolefin elastomers or rubber in the present invention are used for the separate mixing reason described above, instead of an already blended TPO. Any suitable polyolefin elastomer can be used. For example, polybutadiene rubber, ethylene-propylene-diene rubber (EPDM), ethylene-octene copolymers, and other elastomers are useful. Non-limiting examples of such elastomers are those commercially available from multinational companies such as Bayer, Dupont-Dow Elastomers, Uniroyal Chemical, ExxonMobil, and others. ENGAGE™ 8180, ENGAGE™ 8842, and other ENGAGE™ polyolefin elastomers are especially preferred ethylene-octene copolymers available from DuPont Dow Elastomers LLC of Wilmington, DE that function well as impact modifiers for nanoconcentrates of the invention.

Nanoconcentrate pellets of the present invention can be mixed with TPO's to form articles benefiting from a balance of stiffness and toughness properties introduced by the nanoclays therein. The nanoconcentrate can be

diluted or "let-down" in any ratio that one skilled in the art desires to yield as a final nanoclay concentration in the article.

One way of dilution is with a twin-screw extruder from any number of sources or a continuous mixer from Farrel. Further information on this technique is found at www.nanocor.com/tech_sheets/P806.pdf which describes let-down of conventional nanoconcentrates into TPO's.

Another way of dilution is mixing the nanoconcentrate at the point of molding the final article. The mixing inlet for any type of molding machine can be sufficient to disperse the nanoconcentrate of the present invention into the TPO. This is an efficient way to introduce a more expensive concentrate into a final molded product, based on working capital requirements of raw material inventory, because the nanoconcentrate arrives just-in-time.

Usefulness of the Invention

Final molded articles made from TPO are more valuable because nanoclays provide increased stiffness and toughness. Such molded articles can be made into any number of shapes, among them, automobile parts, large appliance parts, and the like.

Further explanation of the invention is found in the following examples.

Examples

Nanoclay-containing concentrates were prepared according to the recipes and commercial sources stated in Table 1 and the mixing conditions stated in Table 2. The concentration of nanoclay and dispersion agent were kept constant with the concentration of polyolefin copolymer rubber being varied.

Table 1
Concentrate Recipes for Use in TPO

Ingredient Wt. %	1	2	3	4
Nanoclay	40	40	40	40
PP-g-MAH	10	10	10	10
EO Copolymer Rubber	15	10	5	0

Table 1				
PP	35	40	45	50

C mmercial Sources		
Ingredient and Use	**Source**	**Brand(s)**
Nanoclay to enhance stiffness	Nanocor	I44p
Ethylene-Octene Copolymer to modify impact	DuPont-Dow	EG8180
PP-g-MAH (maleated polypropylene) to disperse nanoclay	Crompton	PolyBond PBX5104
PP (polypropylene) to serve as concentrate carrier		
TPO (thermoplastic polyolefin)	Basell	CA387; Adflex KS311P; and Pro-Fax SG702

Table 2				
Concentrate Making Conditions				
Example	**1**	**2**	**3**	**4**
Concentrate Mixing Equipment	Werner & Pfleiderer ZSK 25 co-rotating twin screw extruder			
Concentrate Mixing Temperature	200°C			
Concentrate Mixing Speed	1100 rpm			
Order of Addition	All Ingredients except Ethylene-Octene Copolymer are added together, with EO Copolymer added downstream, i.e., after thorough dispersion of nanoclay and dispersion agent in carrier			

After the concentrates 1-4 were made, they were mixed into three different TPO's to simulate the addition of concentrate just prior to molding of the TPO into a useful article.

Table 3 shows the amount of dilution, also known as let-down, along with the test results for stiffness and toughness of the final article.

Table 3				
TPO Compounds				
Example	**Concentrate**	**Wt. Percent**	**TPO**	**Wt. Percent**
Comp. A	--	--	CA387P	100%
5	1	20%	CA387P	80%
6	2	20%	CA387P	80%
7	3	20%	CA387P	80%
8	4	20%	CA387P	80%
Comp.B	--	--	Pro-Fax SG702	100%
9	1	20%	Pro-Fax SG702	80%
10	2	20%	Pro-Fax SG702	80%
11	3	20%	Pro-Fax SG702	80%
12	4	20%	Pro-Fax SG702	80%
Comp. C	--	--	Adflex KS311P	100%

13	1	20%	Adflex KS311P	80%
14	2	20%	Adflex KS311P	80%
15	3	20%	Adflex KS311P	80%
16	4	20%	Adflex KS311P	80%
17	2	10%	Adflex KS311P	90%

Example	**ASTM D790 (PSI)**		**ASTM D3837 (Joules)**					
	Flex. Mod.	**Stress at Yield**	**Inst. Impact Room Temp.**		**Inst. Impact 0°C**		**Inst. Impact -30°C**	
			Peak	**Total**	**Peak**	**Total**	**Peak**	**Total**
Comp. A	120000	3380	16.7	30.7			24.9	45
5	149000	3540	16.8	30.5			24.6	39.3
6	157000	3740	16.6	30.2			22.6	27
7	158000	3850	16.6	29.7			13.8	14.4
8	179000	4110	16.5	28.7			3.9	4.9
Comp. B	155000	4770	18.8	33.8	22.4	41.3		
9	233000	5530	20.1	31.1	24.1	37.4		
10	239000	5650	21.1	30.3	18.5	22.5		
11	244000	5720	20.6	28.5				
12	258000	5980	20.6	24.3	11.5	12.1		
Comp. C	78400	2530	13.8	25				
13	123000	3040	16.1	26.9				
14	130000	3220	15.7	26.4				
15	133000	3330	15.1	26.2				
16	149000	3540	15.4	25.4				
17	109000	3010	15.2	26.4				

Table 3 shows that Examples 5-8, 9-12, and 13-16 (each containing 8 wt. percent nanoclay) consistently outperform the Comparative Examples A, B, and C, respectively, in respect of Flexural Modulus and Stress at Yield. Because each of the Comparative Examples are different types of TPO (A is a rigid TPO; B is an impact copolymer; and C is a flexible TPO), assessment of instrument impact performance is more complex. All of Examples 5-16 exhibit ductility by comparing the peak vs. total instrument impact values. As polyolefin copolymer content decreases, instrument impact performance at the various operational temperatures also decreases. Therefore, the balance of stiffness and toughness is found preferably in Examples 5, 9, and 13.

Examples 14 and 17 compare the amount of nanoclay present in the TPO Compounds of the same ingredients, with Example 14 containing 8% nanoclay and Example 17 containing 4%. Along with Comparative Example C,

a trend line can be established from 0 to 4 to 8 weight percent, with increased stiffness along that line.

The invention is not limited to the above embodiments. The claims follow.

What is claimed is:

1. A method of making a nanocomposite of carrier, nanoclay, polyolefin elastomer and optional nanoclay dispersion agent, comprising the steps of

(a) adding the carrier, nanoclay, and optional nanoclay dispersion agent to an extruder; and

(b) adding the polyolefin elastomer downstream from where the carrier, nanoclay, and optional nanoclay dispersion agent were added.

Nanoconcentrates Containing Polyolefin Elastomer

Abstract

A concentrate of nanoclay, polyolefin carrier, and polyolefin elastomer is disclosed, optionally also containing a dispersion agent for the nanoclay. The nanocomposite is prepared for use with thermoplastic polyolefins (TPO's). The polyolefin elastomer, preferably an ethylene-octene copolymer, is added into a mixing extruder downstream of the other ingredients. The nanoconcentrate contributes increased stiffness and toughness to a TPO, which can be used form molded articles such as automotive parts.

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